

PATENT SPECIFICATION

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(54) MAGNETIC FLUIDS

(71) We, GEORGE W. REIMERS and SANAA E. KHALAFALLA, both Citizens of the United States of America of 2708 Mesa Verde Court, Burnsville, Minnesota 55337, United States of America and 2551—37th Avenue South, Minneapolis, Minnesota 55406, United States of America, respectively, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for making magnetic fluids and for making dispersion agent-coated magnetic particles for forming such fluids.

Magnetic fluids, sometimes referred to as "ferrofluid" in the art, are Newtonian liquids which retain their fluidity in the presence of external magnetic fields and field gradients. The fluids are ultrastable colloidal suspensions of submicron-sized, ferro- or ferri-magnetic particles in liquid carriers such as hydrocarbons, particularly paraffinic hydrocarbons such as kerosene, silicones, fluorocarbons and the like. A definitive test which characterizes magnetic fluids is their super paramagnetic behavior shown by the absence of a hysteresis loop in their magnetization curves. The magnetization curve of a magnetic fluid is in appearance a symmetrical sigmoid curve about the origin.

Magnetic fluids are conventionally produced by long-term grinding techniques such as those disclosed by Papell (U.S. 3,215,572). Since grinding times required by the prior art methods range from days to several weeks, it is readily evident that these methods are cumbersome, costly and ill-suited to any large scale production of magnetic fluids.

These fluids find use in a wide range of applications. They may be used in the separation of particulates according to density by such techniques as are shown in the Rosen- weig patent, No. 3,483,969.

It has also been proposed to use oil soluble magnetic fluids for cleaning up oil spills. A magnetic fluid is added to an oil slick, imparting magnetic properties to the entire

slick, after which the oil-magnetic fluid mixture is collected by means of an electro-magnet. While this is an attractive and promising technique, its development and use has been severely hampered by the high cost of magnetic fluids. A detailed discussion of magnetic fluid properties and uses is found in an article by R. E. Rosenweig published in *International Science and Technology*, July, 1966, pages 48—56.

The present invention provides a process for coating magnetic particles with a dispersing agent which comprises:

forming a slurry or suspension of colloidal size (as herein defined) magnetic particles in water;

coating the surface of particles with an adsorbed layer of a dispersing agent, said dispersing agent being in a water soluble form;

heating the slurry of dispersing agent coated particles to a temperature sufficient to decompose the dispersing agent and to transform it to a non-water soluble form; and

separating from the slurry a fraction comprising dispersing agent coated magnetic particles.

The separated fraction of particles may be dispersed in any non-aqueous liquid medium having solubility for the dispersing agent in its non-water soluble form. The resulting magnetic liquid comprises a stable, colloidal suspension of ferrimagnetic particles.

Alternatively, the non-aqueous medium, or carrier liquid, may be added to the aqueous suspension with the dispersing agent, or after its introduction, to form a magnetic fluid directly. The magnetic fluid may then be decanted from the aqueous phase and further heated to evaporate entrained water. Preferred dispersing agents include the long chain fatty acids; those acids in their ammonium salt form are water soluble but decompose at moderate temperatures to the acid form which is not soluble in water. Preferred carrier liquids include hydrocarbons generally; especially the saturated hydrocarbons of intermediate boiling point range.

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We particularly prefer to precipitate ferrimagnetic iron oxide particles approximating the composition of magnetite.

5 Specific embodiments of our invention will be described with reference to the accompanying drawings in which:

Figure 1 illustrates a magnetization curve typical of our magnetic fluids.

10 Figure 2 depicts the magnetization curve of fluid suspension of magnetic particles.

Figure 3 comprises a diagrammatic flow sheet illustrating one embodiment of our process for the manufacture of magnetic fluids.

15 Figure 4 depicts another embodiment of our process.

Figure 5 diagrammatically represents a process embodiment in which a magnetic gum, or magnetic fluid concentrate, is formed.

20 The traditional approach taken to the manufacture of magnetic fluids has been the long term grinding of the smallest particle size magnetite available. We approached the problem from the opposite viewpoint; instead of making big particles little, we start on molecular scale and grow particles to the
25 desired colloidal size. It is well known that colloidal-size particles of hydrated iron oxides are initially formed when aqueous solutions of iron salts are rapidly neutralized with a base such as sodium or ammonium hydroxide.
30 There is much in the literature of analytical chemistry dealing with techniques to promote growth and coagulation of these colloidal precipitates so as to allow their filtration from liquids without loss. In our process the objectives are diametrically opposite; we maintain the "status quo" of the colloidal particles until they become peptized in the desired dispersion medium.

40 When making a gravimetric determination of iron, the analytical chemist tries to avoid the formation of colloids. Therefore he takes precautions, such as starting precipitation slowly, to insure that an excessive number of nuclei do not form. In this way, each particle
45 nucleus can grow to a relatively large size, thus forming a crystalline precipitate which filters readily. Speed of crystallization and consequently the number of particles formed in a given system, can be controlled to some extent by the manner in which the reactants are mixed. The number of nuclei formed is a function of the amount by which the concentrations of the ions in a solution exceed
50 the equilibrium value at the time precipitation begins. If precipitation is caused to occur very slowly it is possible, at least in theory, to obtain a single crystal.

55 In our invention, we deliberately proceed in a manner opposite the advice given the analytical chemist. We precipitate the iron hydroxides rapidly, under conditions of excessive supersaturation and preferably at room temperature or below. We also avoid the
60 agglomeration of colloidal particles, which

would tend to form a gelatinous mass or gel, so that individual colloidal sized particles may be peptized to form a stable colloidal suspension in a liquid carrier medium.

Like magnetic fluids produced by grinding
65 processes, our magnetic fluids comprise three basic components; colloidal sized magnetic particles, e.g., of magnetite, a dispersing agent coating the individual magnetic particles and
70 a liquid carrier medium compatible with the dispersing agent. Our process for making magnetic fluids comprises the following process steps (1) forming a slurry or suspension of magnetic particles, e.g. by precipitation of
75 an aqueous suspension of colloidal-sized ferrous-ferric oxide particles by the rapid neutralization of a mixed, ferrous-ferric salt solution by addition of a relatively strong base; (2) coating the precipitated particles, e.g. ferrous-ferric oxide particles in the water
80 phase with a dispersing agent; (3) heating the coated particles to convert the dispersing agent into non water soluble form; and (4) optionally forming the magnetic fluid by dispersing the particles in water.

85 The first step is well known in the art. Precipitation may be accomplished using any relatively strong base but use of ammonium hydroxide is very much preferred. Dispersing agents useful in step 2 must fulfil several
90 criteria; they must form an adsorbed coating on the surface of each magnetite particle sufficient to overcome the attracting force between particles which would otherwise produce
95 flocculation, they must react with a cation to form a water soluble salt or soap and that water soluble salt or soap must decompose at relatively moderate temperatures to form a water-insoluble coating around each
100 magnetite particle.

105 All of these criteria are met by a number of organic compounds which contain the carboxyl group, COOH. A preferred grouping of dispersing agents includes the fatty acids. Our most preferred group of dispersing
110 agents comprises fatty acids having approximately 18 carbon atoms. Oleic, linoleic and linolenic acids, for example, give excellent results, are readily available in quantity and are relatively low in cost. It is not
115 necessary to use pure compounds. Mixtures of fatty acids and other compounds containing the carboxyl group are readily available in the form of tall oils produced by the Kraft paper process. The by-products of these oils
120 may be used as dispersing agents in our process and in some cases are preferred.

125 Fatty acids and similar compounds are insoluble in water. However, these same compounds form a salt or soap with cations such as ammonium or sodium which in turn are water soluble. The sodium salts or soaps are relatively temperature stable and are generally useless for our purposes. Ammonium salts or soaps are much less thermally
130

stable and are strongly preferred. Ammonium oleate, for example, begins to decompose at 78°C with the evolution of ammonia gas.

After the precipitation of a colloidal suspension of iron oxide particles, the dispersing agent is added with heating. It is preferred to add the dispersing agent to the aqueous suspension at a temperature above 70°C. The dispersing agent at this stage of the process must be in the form of its water soluble ammonium salt. When the precipitation is accomplished using an excess of ammonium hydroxide, as is preferred, the dispersing agent will form the corresponding ammonium salt by reacting with excess ammonium hydroxide contained in the solution. However, if some other base, such as sodium hydroxide is used for the precipitation step, then excess base must be removed from the slurry of precipitated iron oxides and ammonium hydroxide added prior to or with the introduction of the dispersing agent. Alternatively, the dispersing agent may be added in the ammoniated form, as ammonium oleate for instance, but it is preferred to operate with an excess of ammonium ion in solution at this stage of the process.

The ammoniated dispersing agent is adsorbed, probably as a mono-molecular layer, on the surface of the oxide particles. Heating of the reaction mix is continued to a temperature level above the decomposition temperature of the ammoniated dispersing agent. At those temperatures, generally in the range of 70° to 100°C, ammonia generated by decomposition of the ammoniated dispersing agent is expelled from the solution as a gas thus making the decomposition reaction go essentially to completion. As a result, there is produced a suspension of iron oxide particles individually coated with a layer of dispersing agent in its original form. For example, when oleic acid is used as a dispersing agent, ammonium oleate is produced by reaction with ammonium hydroxide contained in the precipitated iron oxide slurry. Iron oxide particles are coated with ammonium oleate and, upon further heating, the ammonium oleate decomposes releasing ammonia gas thus changing the particle coating to oleic acid.

As the dispersing agent decomposes, there occurs a coagulation of the individually coated particles to form a wax-like mass which tends to separate from the water phase. This wax-like mass or coagulum is essentially a magnetic fluid concentration since, after water removal, it will form a magnetic fluid upon mixing with non-aqueous liquid carriers which display at least some solubility toward the dispersing agent. A wide variety of liquid carriers, or magnetic fluid mediums, may be used. These include the general class of hydrocarbons, silicone oils, many of the fluorocarbons and like compounds. Hydro-

carbons are generally preferred as the carrier liquid since they combine the characteristics of dispersing agent compatibility, water immiscibility, low viscosity and economy which are important for most magnetic fluid applications. Among the hydrocarbons, liquid fractions of intermediate boiling point range such as kerosene and fuel oils are especially appropriate as the carrier liquid for magnetic fluids used in separatory processes.

Instead of adding a dispersing agent only to the iron oxide suspension, the dispersing agent may be added in admixture with the liquid carrier medium. In this embodiment, magnetic iron oxide particles are extracted from the water phase into the carrier liquid phase as the ammoniated dispersing agent decomposes. As decomposition is completed, there is formed a two phase system; an aqueous phase containing ammonium salts of the iron compound used and a non-aqueous magnetic fluid phase. The two phases may then be separated by settling and decantation to recover the magnetic fluid product.

Iron salts used as raw materials for our process must be water soluble. Preferred salts are the chlorides and sulfates because of their availability and economy. Presence of other metal ions, including those of manganese, chromium, nickel and copper are not detrimental provided that those other metal ions are present in relatively small amount. We particularly prefer industrial waste streams containing iron compounds as our source of raw material. Such waste streams are available in large volume at essentially no cost as by-products of steel pickling or etching operations and from the sulfate process for the production of titanium dioxide pigments. Magnetic fluids produced from pickling liquors, for example, were indistinguishable in characteristics from those produced using reagent chemicals.

Concentration of magnetic iron oxides in the magnetic fluids may be varied at will depending upon properties desired. As magnetite concentration within the fluid increases, so also does the saturation magnetization, viscosity and specific gravity. For most uses of magnetic fluids, a magnetite concentration ranging from 5 to 50 grams magnetite per 100 ml fluid will be satisfactory. For example a magnetic fluid containing 5 g magnetite per 100 ml fluid will display a saturation magnetization of 40 to 45 gauss while a fluid containing 50 g magnetite per 100 ml fluid will display a saturation magnetization of about 425 gauss. Viscosity and specific gravity can be varied, at least to some extent, independently of magnetite concentration by selection of carrier liquids or mediums.

The amount of dispersing agent required is not critical so long as there is enough to coat individual magnetic particles sufficiently

to prevent agglomeration. Excess dispersing agent merely dissolves in the carrier liquid but large excesses are undesirable because of the increased viscosity produced in the magnetic fluid. Flocculation of the magnetic particles may also occur as a result of such excesses. On a weight basis, 0.05 to 0.75 g dispersing agent per g magnetite is satisfactory. We prefer in most instances to formulate magnetic fluids containing from 0.1 to 0.5 g dispersing agent per g magnetite.

As the term is used in this specification, magnetite includes all those ferroso-ferric oxides having ferromagnetic properties. It is not limited to the ideal molar ratio implied by the oxide formula $\text{FeO} \cdot \text{Fe}_2\text{O}_3$. Colloidal size particles, as the phrase is used in this specification, is restricted to particles sufficiently small so as to not settle when dispersed in a liquid even under the influence of artificially high gravitational or magnetic fields. In terms of particle diameter, colloidal particles are typically in the order of 100 Angstroms or less in size.

Referring now to Figure 1, there is shown a magnetization curve typical of that obtained from our magnetic fluids. Figure 2 is a magnetization curve typical of that displayed by magnetic particles suspended in a liquid. In both figures, magnetic induction B is plotted as the ordinate while the magnetic field, H, is plotted as the abscissa. As shown in Figure 1 the magnetization curve 1, obtained from magnetic fluids consists of a symmetrical sigmoid curve about the origin. In contrast, the magnetization curve 2, obtained from a suspension of magnetic particles, displays the hysteresis loop characteristic of ferrimagnetic materials. The characteristic sigmoid magnetization curve constitutes a definitive test for the identification of a magnetic fluid.

A diagrammatic flow sheet illustrating one technique for manufacturing magnetic fluids is shown as Figure 3. A reactor of vessel 10, preferably equipped with stirring means 11 is utilized to conduct a rapid precipitation reaction. A ferrous salt 12 and a ferric salt 13, both preferably in aqueous solution and in a molar ratio approximating 1:2, are introduced into vessel 10 where they are co-precipitated in an excess of ammonium hydroxide introduced via line 14. Precipitation must be accomplished rapidly in an excess of ammonium hydroxide in order to obtain maximum production of colloidal-size hydrated iron oxide particles. Preferably the precipitation is carried out at room temperature or below in order to avoid excessive coagulation or growth of the particles.

An aqueous slurry of the very finely divided oxide particles is then transferred via conduit 15, to a second reactor or vessel 16 also equipped with stirring or agitation means 17. A dispersing agent 18, such as oleic

acid, and a solvent 19, such as kerosene, are introduced into vessel 16 and mixed with aqueous slurry 15. It is important to note that slurry or suspension 15 must contain sufficient ammonium hydroxide to completely react with dispersing agent 18 and form what essentially is an ammonium soap. Alternatively, dispersing agent 18 may be pre-reacted with ammonium hydroxide, in which case the ammonium hydroxide content of slurry 15 may be reduced to a level slightly above that stoichiometrically required to precipitate the mixed ferrous and ferric hydrous oxides.

The dispersing agent functions to coat individual particles of the hydrous iron oxide and arrest further agglomeration and growth of the particles. Since the ammoniated dispersing agent is water soluble, this coating action takes place primarily in the water phase. The combined reactants within vessel 16 are heated, preferably quite rapidly, to a temperature above the decomposition temperature of the ammoniated dispersing agent. This is generally a temperature above 75°C. For example, ammonium oleate decomposes at a temperature of 78°C, and when using oleic acid as a dispersing agent, the reaction mixture must be heated to a temperature above 80°C and preferably above 90°C. Heating decomposes the ammoniated dispersing agent and free ammonia is released which is driven from solution, along with excess ammonia contained in slurry 15, and is vented from vessel 16 by means of conduit 20. Ammonia may be recovered for recycle from stream 20 by a water scrub or stream 20 may be recycled directly back to vessel 10.

Decomposition of the ammoniated dispersing agent has a drastic effect upon its solubility characteristics. The dispersing agent is no longer soluble in water but is soluble in hydrocarbons and similar liquids. Hence there occurs a transfer of dispersing agent-coated iron oxide particles from the aqueous phase to the solvent phase. Another result of heating is the development of the magnetite structure from the co-precipitated hydrous ferrous and ferric oxides. There is some indication that magnetite will develop at temperatures as low as 50°C but, in any event, the transformation proceeds nicely within the temperature range required to decompose the ammoniated dispersing agent.

At this stage, the reaction mixture within vessel 16 comprises a suspension of dispersing agent-coated, colloidal-size particles of magnetite in the solvent phase and an aqueous salt solution as a second phase. The mixed phases are passed via line 21 to separator vessel 22 where the phases are allowed to separate. Top phase 23 will usually comprise the suspension of magnetite in solvent since most solvents used in our process have

specific gravities less than 1. Bottom phase 24 comprises an aqueous salt solution which may be discarded via line 25 or evaporated for recovery of the contained salt. The top phase is passed via conduit 26 to heater means 27 where the magnetic fluid, still containing small quantities of suspended and dissolved salt and water, is raised in temperature to facilitate the final dehydration. This heated mixture is then passed by way of means 28 to magnetic decanter 29. A localized magnetic field is applied to an area of decanter 29 as by use of an appropriate permanent or electromagnet 30. The magnetic field causes magnetic fluid to accumulate in a mass 31 within the magnetic field where it is drawn off by tapping means 32. Water and salt are voided from the decanter by way of line 33. As may be appreciated from the flow sheet and description, this embodiment of our process may be operated on a batch, semi-continuous or a continuous basis.

Figure 4 illustrates another embodiment of our process. In this mode, we operate on a batch or semi-continuous basis. A closed vessel 40 equipped with stirring or agitation means 41 is provided to carry out the reaction. An aqueous iron containing stream is first introduced into vessel 40. This stream in turn comprises a ferrous salt stream 42 and a ferric salt stream 43 which are merged and mixed prior to or after introduction into the vessel. Ratio of ferrous to ferric iron preferably closely approximates that of magnetite. An excess of ammonium hydroxide is then introduced into the reaction vessel via means 44 with agitation to precipitate iron hydroxides. This reaction is exothermic and a substantial rise in temperature of the liquid within reactor 40 will occur. A dispersing agent 45, preferably in admixture with a solvent 46 is then added to the reaction mix with continued agitation. The reaction mix within vessel 40 is further heated by any convenient means (not shown) until the temperature of the mix is above, and preferably at least 10°C above, the decomposition temperature of the ammonium salt of the dispersing agent.

The reaction mix, now comprising a colloidal suspension of magnetite in solvent and ammonium salt in water, is passed via conduit 47 to distillation means 48. There, the excess ammonia and water is removed as overhead stream 49. A magnetic fluid product stream 50 is also recovered from the distillation means 48 leaving a solid residual salt fraction 51. It is to be noted that this embodiment of our process requires the solvent used to have a higher boiling point than water. Solvents such as kerosene are appropriate for use in this embodiment. Alternatively, a magnetic decanter such as was illustrated in Figure 3, may be used to separ-

ate magnetic fluid from the water phase in place of distillation means 48.

Figure 5 illustrates an embodiment of our process which we generally consider to be the most versatile since any compatible solvent may be used as a base for the magnetic fluid. There is provided a reaction vessel 60 with agitation means 61 into which is introduced an aqueous solution of iron salt. These iron salts preferably comprise a ferrous salt 62 and a ferric salt 63 in a ratio approximating that of magnetite. A stream of ammonium hydroxide 64, preferably in concentrated form, is added to the mixed ferrous-ferric salt solution with agitation to precipitate iron oxides and hydroxides. Ammonium hydroxide is added in excess of that required for the precipitation.

The suspension of colloidal size iron oxides is then transferred via conduit 65 to a second reaction vessel 66 also equipped with agitation means 67. A dispersing agent 68 is added to the suspension and the mixture is heated with agitation to a temperature above the decomposition temperature of the salt formed by reaction of the dispersing agent with excess ammonia contained in stream 65. Upon decomposition of the ammoniated dispersing agent, a gum-like material forms which comprises dispersing agent-coated magnetite particles. Excess ammonia is vented from vessel 66 by way of means 69. The coagulum-water-ammonium salt mixture is then passed to settling or decanting vessel 70 by way of transfer means 71. In vessel 70, the coagulum, or magnetic gum, settles to the bottom since it has a relatively high specific gravity due to its magnetite content. A water stream containing dissolved salts 72 is decanted from the top of vessel 70 while a magnetic gum fraction 73 is removed from a lower point in the vessel. The last traces of entrained water are removed from the magnetic gum in drier means 74; the water being vented at 75.

A dried magnetic gum fraction 76 is recovered from drier means 74 and this may constitute the product of our process. Alternatively, the magnetic gum may be passed to a mixing or dispersing means 77 and a solvent 78 added to form a magnetic fluid product 79. Magnetic gum 76 may be considered to be a magnetic fluid concentrate and in this form offers advantages over the prepared magnetic fluid. For example, the magnetic gum may be dispersed in any one of a large variety of solvents. Transportation and storage advantages are obvious.

The process of Figure 5 has been illustrated and described as operating on a semi-continuous or continuous basis. It may also be operated on a batch basis in which all of the processing steps are carried out within the same processing vessel.

Our invention is further explained and illustrated by the following examples.

Example 1

A laboratory technique for the production of small quantities of magnetic fluids having reproducible characteristics has been developed. This is a "recipe" type of procedure which can be accomplished using simple apparatus and open beakers.

0.09 mole of ferric chloride and 0.06 mole of ferrous chloride are dissolved in 50 ml of distilled water. The mole ratio of ferric to ferrous iron (3 to 2) is smaller than that of magnetite (2 to 1). However, during the reaction, some ferrous iron oxidizes to ferric since the reaction is performed in open vessels. 50 ml of concentrated (28%) ammonium hydroxide are slowly added while stirring to precipitate the iron hydroxides. The mixture is heated to 95°C and 50 ml of Fisher odorless kerosene and 5 ml of Mallinckrodt U.S.P. oleic acid are added with rapid stirring. Heating is continued and a distinct phase separation occurs between the aqueous and organic portions.

The aqueous phase is removed using a pipette. This reduces the heating time for water removal and also eliminates most of the ammonium chloride residue. Heating is continued until the water has evaporated and the temperature of the organic phase is allowed to rise to 130°C.

The fluid is cooled to room temperature and poured into a graduate. Kerosene is added to adjust the fluid volume to 55 ml; this compensates for kerosene lost during heating. The fluid is vacuum filtered using Whatman No. 31 paper and over-sized particles (if any) are removed from the fluid with a magnet.

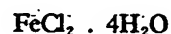
A fluid prepared by this method has the following nominal specifications: (1) saturation magnetization of 140 gauss at 7000 oersteds applied field; (2) a specific gravity of 0.92 g/cc; (3) a viscosity of 2.23 centipoise measured using an Ostwald type capillary viscometer at 25°C. It is emphasized that this specific procedure is designed for the production of experimental quantities of magnetic fluid having reproducible characteristics and does not necessarily represent a preferred method of manufacture.

Example 2

Six batches, each containing 0.04 mole of



and 0.02 mole of



were dissolved in water. Ammonium hydroxide was used to precipitate the colloidal

iron hydroxides. Each batch of precipitate was decanted to a volume of 75 ml.

An electric fry pan was used to heat 300 ml of the kerosene/2% oleic acid carried fluid to 110°C. An argon atmosphere was maintained over the kerosene to prevent ignition. A Jet-Pac aerosol-type sprayer was then used to spray the aqueous suspension of hydroxides onto the kerosene. With each spray burst of hydroxide, the carrier fluid darkened, indicating the particles were going into suspension. When the spraying of a batch was completed, the fluid was cooled to room temperature. As only part of the water was lost by evaporation, the remainder, with its dissolved ammonium chloride, was removed by decantation. Some kerosene was lost by evaporation and fresh kerosene was added to return the fluid volume to 300 ml. This operation was repeated until the six batches had been sprayed.

To speed the settling of the oversized particles, a beaker containing the fluid was placed near the poles of a permanent magnet where a pipette was used to draw the fluid from the sediment. Kerosene was added to this fluid to return the volume to 300 ml.

The specific gravity of the fluid was 0.84 g/cm³ as compared to 0.77 g/cm³ for pure kerosene at the same temperature. Using this fluid it was possible to levitate copper balls of specific gravity 8.96 g/cm³ with an electromagnet at a power setting of 3 kilo-oersted (koe) and having a one-half-inch pole piece gap.

Example 3

A portion of the fluid from example 2 was evaporated at 110°C until its volume was halved. Argon was flowed over the fluid to prevent ignition. This concentrated fluid had a specific gravity of 0.85 g/cm³. It was possible to levitate lead of specific gravity 11.35 g/cm³ and a platinum wire of specific gravity of 21.45 g/cm³ using power settings of 7.5 and 14.5 koe, respectively, for an electromagnet with a half-inch pole gap.

Example 4

For this example 0.2 mole of



and 0.1 mole of



were dissolved in water and precipitated with excess ammonium hydroxide. Water was decanted until the volume of the aqueous precipitate was 200 ml. Two hundred milliliters of kerosene containing 2 percent oleic acid were heated to 110°C in a stainless steel beaker. The beaker was fitted with a drain tube to facilitate water removal.

In this example the aqueous suspension of magnetic material was simply poured, in small amounts, onto the heated kerosene. Peptization of the magnetic material occurred as in example 2. Because the water that was not boiled away was heavier than the kerosene carrier fluid, it settled to the bottom of the beaker and was drained away.

After adding all of the magnetic material, the fluid was cooled to room temperature. A large permanent magnet was used to speed settling of the larger particles and the fluid was drawn off with a pipette. The fluid was then evaporated to 50 ml at 110°C using argon gas to prevent ignition. This resulted in a magnetic fluid having a specific gravity of 0.95. It was possible with this fluid to levitate an alumina ball having a specific gravity of 3.9 g/cm³ using a small laboratory permanent magnet whose field gradient was a little less than 800 Oersted/cm.

Example 5

In this example 0.2 mole of



and 0.1 mole of



were dissolved in water, cooled and the hydrous oxides rapidly precipitated with excess ammonium hydroxide. Then 20 ml of oleic acid and 40 ml of kerosene were added while stirring to the aqueous solution of precipitate. The mixture was then heated, under argon, in a stainless steel pan to evaporate the water. When evaporation was complete, the fluid temperature was allowed to rise to 120°C, held at this point for five minutes, and then cooled to room temperature.

The resulting fluid was poured into a beaker leaving a deposit of ammonium chloride in the pan. The magnetic particles in the

fluid were then flocculated by the addition of 250 ml of acetone. A magnet was used to pull the magnetic flocculate to the bottom of the beaker while the supernatant liquid was poured away. A second addition of 200 ml acetone was used to wash the flocculate of excess oleic acid.

After pouring away the acetone, the flocculate in the beaker was converted to a colloidal solution by adding kerosene to make the fluid volume 100 ml. The fluid was heated to 100°C under argon to evaporate any traces of acetone. Finally, the beaker of fluid was placed near the poles of a large permanent magnet and a pipette was used to draw the fluid away from the over-sized particles.

Magnetic fluid made by this technique had a specific gravity of 0.96 and it was possible to levitate an alumina sphere of specific gravity of 3.9 g/cm³ using a small laboratory permanent magnet.

Example 6

A grinding experiment was performed to compare the fluids prepared in the previous examples with a fluid made by ball-milling. One hundred and eighty-five grams of magnetite from Electronic Space Products, Inc., having a surface area of 7.02 m²/g was ground for 100 hours. The magnetite was charged into a 1.3 gallon laboratory ball mill with 7.35 kilograms of 1/4-inch steel balls and 1 liter of kerosene containing 2 percent oleic acid. The fluid had a specific gravity of 0.79 when measured 48 hours after completion of grinding.

A vibrating sample magnetometer was used to compare the saturation magnetic moments per unit volume of the foregoing magnetic fluid preparations. As a criterion for the fluid magnetic strength, we measured the moment at 7 koe field strength and the results are shown in table 1. It is evident that the fluid prepared by peptization in example 4 is about 20 times as strong as the fluid prepared by grinding (example 6).

TABLE 1

	Magnetic fluid in example number	Scale reading microvolts at 7 koe	Magnetic induction I=4 M, gauss	Magnetization, M, moment/unit volume (gauss)	Sample moment relative to moment of example 6.
90	2	749	18.28	1.45	2.79
	3	1400	34.16	2.72	5.23
	4	5200	126.88	10.09	19.40
95	5	4180	101.99	8.11	15.60
	6	270	6.59	0.52	1.00

Example 7

A mixture of iron salts containing 0.45 mole of ferric chloride and 0.30 mole of ferrous chloride were precipitated in an open vessel using excess ammonium hydroxide. The precipitated mixture was heated to 90°C and

25 ml of oleic acid, alone, was added. Heating was continued until decomposition of ammonium oleate was complete as evidenced by a cessation of ammonia evolution. A gum-like mixture formed comprising oleic acid-coated magnetic particles. This coagulum was

then removed from the ammonium chloride solution and any entrained water was evaporated by further heating.

Four fluids were prepared by mixing 22 gram quantities of the oleic acid coated mag-

netic particles with 50 ml of either pentane—bp. 35°C; hexane—bp. 68°C; n-heptane—bp. 98°C; or kerosene—bp. >180°C. The saturation magnetization M_s , density, and viscosity of these fluids are given as follows:

TABLE 2

Carried fluid	M_s , gauss	Density, g/ml	Viscosity centipoise
Pentane	160	0.785	0.361
Hexane	170	0.836	0.491
n-Heptane	170	0.848	0.702
Kerosene	190	0.938	2.352

Example 8

The relationship between saturation magnetization and magnetite concentration of magnetic fluids was investigated. For the system of magnetite in kerosene using oleic acid as a dispersing agent, it was found that saturation magnetization was a linear function of magnetite concentration. For each 10 g of magnetite dispersed in 100 ml of fluid, the saturation magnetization increased

approximately 85 gauss. This linear relationship held true over the entire range investigated; from 0 to 50 g magnetite per 100 ml of magnetic fluid.

Example 9

A quantity of waste pickling liquor was obtained from a steel mill and a partial chemical analysis was performed. The results are as follows reported in g/l.

TABLE 3

Fe (Total)	Fe ²⁺	Mn	Cr	Ni	Cu	Free HCl
99.98	98.07	0.41	0.008	0.015	0.013	30.20

The pickle liquor was evaluated as a source of ferrous salt in the production of magnetic fluids using the procedure set out in Example 1. Thirty-four ml of waste pickle liquor was substituted for the ferrous chloride normally used. Since free hydrochloric acid was present in the pickle liquor, the volume of ammonium hydroxide used for precipitation was increased from 50 to 55 ml. The saturation magnetization of the magnetic fluid produced was in excess of 140 gauss and was essentially indistinguishable from fluids produced using reagent grade chemicals.

Example 10

In this example, the pickle liquor of Example 9 was used as the source of both ferrous and ferric iron to synthesize magnetic fluids by the technique of Example 1. Ferric chloride was produced by oxidizing the ferrous iron in the pickle liquor with hydrogen peroxide. Excess hydrogen peroxide was removed from the oxidized solution by boiling. Oxidized pickle liquor in the amount of 51 ml was mixed with 34 ml of pickle liquor in the "as received" state. Precipitation was accomplished using 55 ml of ammonium hydroxide. Saturation magnetization of the magnetic fluid produced was in excess of 140 gauss. It could not be distinguished in physical properties from the magnetic fluids produced in Examples 1 and 9.

Example 11

The procedure of Example 1 was repeated

except that a stoichiometric quantity of ammonium hydroxide was used to precipitate the ferrous-ferric oxide. When the kerosene-oleic acid mixture was added to the precipitate, magnetic fluid failed to form. It was postulated that the oleic acid remained in the kerosene phase and did not act as a dispersant for the colloidal iron oxide particles. An additional amount of ammonium hydroxide was then added to the mixture. A magnetic fluid immediately formed. It is believed that oleic acid reacted with the additional or excess ammonium hydroxide to form ammonium oleate which is water soluble but not hydrocarbon soluble. Ammonium oleate, now soluble in the water phase, was then adsorbed on the surface of the colloidal magnetite particles and, since the temperature of the mixture was above the decomposition temperature of the ammonium oleate, decomposed to again form oleic acid. Since oleic acid is soluble in hydrocarbons but not in water, magnetite particles coated with adsorbed oleic acid are extracted into the hydrocarbon phase thus forming a magnetic fluid.

Example 12

The procedure of Example 1 was repeated except that an excess of sodium hydroxide, instead of ammonium hydroxide, was used to precipitate the ferrous-ferric oxide. Upon addition of the kerosene-oleic acid mixture, a magnetic fluid failed to form. Sodium oleate, although soluble in water, will not decom-

pose at low to moderate temperatures as does ammonium oleate. Hence, magnetite particles having an adsorbed oleic acid coating are not produced thus preventing the formation of a magnetic fluid.

WHAT WE CLAIM IS:—

1. A process for coating magnetic particles with a dispersing agent which comprises:

forming a slurry or suspension of colloidal size (as herein defined) magnetic particles in water;

coating the surface of particles with an adsorbed layer of a dispersing agent, said dispersing agent being in a water soluble form;

heating the slurry of dispersing agent coated particles to a temperature sufficient to decompose the dispersing agent and to transform it to a non-water soluble form; and

separating from the slurry a fraction comprising dispersing agent coated magnetic particles.

2. A process as claimed in Claim 1 wherein the colloidal magnetic particles are obtained by reacting an aqueous solution of ferrous and ferric iron salts with a base to form magnetic iron oxide.

3. A process as claimed in Claim 2 wherein the base is an excess of ammonium hydroxide.

4. A process as claimed in any preceding claim wherein the dispersing agent in its water soluble form is an ammonium salt of a long chain fatty acid, and in its non-water soluble form is the corresponding carboxylic acid.

5. A process as claimed in Claim 4 as dependent on Claim 3 wherein the ammonium salt of the long chain fatty acid is formed *in situ* by adding a long chain fatty acid to the iron oxide slurry.

6. A process as claimed in any of Claims 2 to 5 wherein the ratio of ferrous to ferric ions contained in the iron salt solution approximates that in magnetite.

7. A process as claimed in any of Claims 2 to 6 wherein the iron salts are chlorides or sulfates.

8. A process as claimed in any of Claims 2 to 7 wherein the aqueous solution of iron salts is prepared from an industrial waste stream containing ferrous salts, by oxidizing a portion of the ferrous iron in the stream to ferric iron.

9. A process for making a magnetic fluid (as hereinbefore defined) wherein a dispersing agent-coated magnetic particle fraction produced by a process as claimed in any of claims 1 to 8 is further heated to separate entrained water and is thereafter dispersed in a non-aqueous carrier liquid to form a magnetic fluid.

10. A process as claimed in Claim 9 wherein the carrier liquid is a hydrocarbon.

11. A process as claimed in Claim 9 or 10 wherein the magnetic fluid has a saturation magnetization in the range of 50 to 500 gauss.

12. A process for making a magnetic fluid (as hereinbefore defined) wherein a carrier liquid is added to a slurry of magnetic particles coated with dispersing agent in its water soluble form, said carrier liquid being immiscible in water and having a solubility for the dispersing agent in its non-water soluble form and heating said slurry, whereby magnetic particles coated with dispersing agent in its non-water soluble form are transferred from the water slurry to the carrier liquid and thereby form a magnetic fluid.

13. A process as claimed in Claim 12 wherein the carrier liquid is a hydrocarbon and wherein the dispersing agent comprises oleic acid.

14. A process as claimed in Claim 13 wherein the hydrocarbon is kerosene or a fuel oil and the magnetic fluid contains from 5 to 50 grams of ferrimagnetic iron oxide particles per 100 milliliters of magnetic fluid.

15. A process as claimed in Claim 14 wherein the magnetic fluid contains from 0.05 to 0.745 grams of oleic acid per gram of iron oxide.

16. A process as claimed in Claim 1 substantially as hereinbefore described with reference to any one of Examples 1 to 5, 7 and 9 to 11.

17. Magnetic fluids or dispersing agent-coated colloidal sized magnetic particles when produced by a process as claimed in any of the preceding claims.

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